

133



Publication number: **0 465 756 A1**

EUROPEAN PATENT APPLICATION

Application number: **91101130.2**

Int. Cl.⁵: **B41M 5/40**

Date of filing: **29.01.91**

Priority: **09.07.90 JP 181246/90**
26.09.90 JP 256265/90

Date of publication of application:
15.01.92 Bulletin 92/03

Designated Contracting States:
DE FR GB

Applicant: **HONSHU PAPER CO., LTD.**
12-8, Ginza 5-chome
Chuo-ku Tokyo(JP)

Inventor: **Moronuki, Katsumi**
4-10-24, Naka-machi
Koganei-shi, Tokyo(JP)
Inventor: **Sasaki, Keiji**
Higashi-Shinozaki, Edogawa-ku
Tokyo(JP)
Inventor: **Nishio, Nobuyuki**
28-6, Akao-cho, Otsu-shi
Shiga-ken(JP)

Representative: **Vossius & Partner**
Siebertstrasse 4 P.O. Box 86 07 67
W-8000 München 86(DE)

Heat-sensitive recording medium.

A heat-sensitive recording medium comprises, on a support, a heat-sensitive recording layer comprising a leuco compound and an organic acid capable of coloring upon contact with the leuco compound, wherein the back of the support is coated with an agent for lowering the electric resistance which comprises a guanidine salt or guanidine derivative salt singly or in combination with cationic polymer having a quaternary ammonium group. The heat-sensitive recording medium has a low electric resistance and therefore, it is free from troubles in feeding or discharging thereof from the recording machine and also from impairment of the thermal head.

EP 0 465 756 A1

BEST AVAILABLE COPY

The present invention relates to a heat-sensitive recording medium. In particular, the present invention relates to a heat-sensitive recording medium free from troubles caused when it is fed into a recording machine or removed therefrom and capable of preventing impairment of the printing part, particularly the thermal head.

5 In conventional recording processes, a thermal energy is applied to a heat-sensitive layer of a heat-sensitive recording medium prepared usually by dispersing a leuco compound and an organic acid in a suitable water-soluble binder and applying thus obtained dispersion to a support such as a paper sheet to form a layer so as to melt the organic acid and to conduct the catalytic reaction, thereby forming a color image. Such a heat-sensitive recording medium is widely used for facsimiles, printers and ticket-selling
10 machines, since the recording machine can be relatively easily maintained.

In recording machines such as facsimiles and printers, a heat-sensitive recording medium is printed and cut by passing it through a printing part, automatic cutter, etc. and then discharged. In the course of this process, the recording medium is usually passed through one or several pairs of guide rolls made of an insulating material such as a rubber or a rigid plastic. In order to make the paper discharge sure, the paper-
15 discharge roll made of an insulating material such as rubber is arranged after the automatic cutter and it is rotated at a peripheral speed higher than that of the paper-passing speed. Further, recently, the speed of the heat-sensitive recording process has remarkably been increased. Namely, the printing/heating time which was around 6 m sec is now 1 to 2 m sec because of technical improvement of the recording apparatus including thermal head and driving circuit. In such an apparatus, the recording medium which
20 was printed and cut while its surface and back are abraded is discharged and, therefore, under a low humidity condition, it is electrostatically charged and sticks to the recording apparatus to make the discharge of the medium impossible. Even in a recording apparatus having no paper-discharge roll, the recording medium is electrostatically charged because of the abrasion thereof between the ordinary guide rolls arranged before the automatic cutter and, as a result, it sticks to the recording apparatus to make
25 passing of the medium impossible. In an extreme case, the thermal head is impaired. Another problem is that a contaminate attached to the surface of the heat-sensitive recording medium by the electrostatic charge caused by the abrasion causes lack of the dots and makes the formation of a clear image impossible.

Methods for preventing the troubles in the passage or discharge of the medium under the low humidity condition, impairment of the thermal head and lack of the dots were proposed. They include, for example, a method wherein a large amount of an electroconductive ion such as sodium is incorporated into the heat-sensitive recording layer to increase the electroconductivity and a method wherein a coarse pigment is incorporated into the heat-sensitive recording layer to reduce the electrostatic charge due to the abrasion. However, in these processes, the thermal head is abraded, and when the recording apparatus having the
35 paper discharge rolls is used, the roll is brought into contact with the back of the recording medium so as to protect the heat-sensitive recording layer. The problems are thus not solved.

To solve these problems, various processes were proposed. In these processes, an agent for lowering the surface electric resistance is used for lowering the surface electric resistance of both surfaces of the heat-sensitive recording medium to a specified value.

40 Japanese Patent Unexamined Published Application (hereinafter referred to as "J.P. KOKAI") No. 57-170794 discloses that although inorganic salts, anionic polymeric electrolytes, electroconductive metal compounds such as electroconductive zinc oxide and tin oxide, alumina sol and silica gel are preferred as the agent for lowering the surface electric resistance, cationic polymeric electrolytes cause a phenomenon called "fog of background" wherein the whole heat-sensitive recording layer is colored with time and when
45 a nonionic polymer is used, the coloring properties are impaired by desensitizing effect of the polymer to reduce the commercial value thereof.

Further, it has been found that when a cationic conducting agent is used for lowering the surface electric resistance, the fog of the background is caused and that when an anionic polymeric electrolyte or inorganic salt is used for lowering the surface electric resistance, the thermal head is broken.

50

Summary of the Invention

Under these circumstances, a primary object of the present invention is to provide a heat-sensitive recording medium which can be smoothly passed through or discharged from a heat-sensitive recording machine such as facsimile or printer having any guide roll mechanism to obtain a print without impairing the coloring properties of the recording paper or damaging the thermal head even under a low humidity condition.

This and other objects of the present invention will be clear from the following description and

Examples.

To solve the above-described problems, the present invention provides a heat-sensitive recording medium comprising, on a support, a heat-sensitive recording layer comprising a leuco compound and an organic acid capable of coloring upon contact with the leuco compound, characterized in that the back of the support is coated with an agent for lowering the surface electric resistance which comprises a guanidine salt or guanidine derivative salt, or a combination of the salt and a cationic polymer having a quaternary ammonium group.

Description of the Preferred Embodiments

The supports usable in the present invention include wood-free papers, medium-quality papers, coated papers, regenerated papers including waste papers and non-woven fabrics.

The leuco compounds usable for producing the heat-sensitive recording papers of the present invention include, for example, triarylmethane dyes such as 3,3-bis(p-dimethylaminophenyl)-6-dimethylaminophthalide, 3,3-bis(p-dimethylaminophenyl)phthalide, 3-(p-dimethylaminophenyl)-3-(1,2-dimethylindol-3-yl)-phthalide, 3-(p-dimethylaminophenyl)-3-(2-methylindol-3-yl)phthalide, 3,3-bis-(1,2-dimethylindol-3-yl)-5-dimethylaminophthalide, 3,3-bis(1,2-dimethylindol-3-yl)-6-dimethylaminophthalide, 3,3-bis(9-ethylcarbazol-3-yl)-6-dimethylamino-phthalide, 3,3-bis(2-phenylindol-3-yl)-6-dimethylaminophthalide and 3-p-dimethylaminophenyl-3-(1-methylpyrrol-3-yl)-6-dimethylaminophthalide; diphenyl-methane dyes such as 4,4'-bis-dimethylaminobenzhydryl benzyl ether, N-halo-phenyl Leucoauramines and N-2,4,5-trichlorophenyl Leucoauramine; thiazine dyes such as Benzoyl Leucomethylene Blue and p-Nitrobenzoyl Leucomethylene Blue; spiro dyes such as 3-methyl-spiro-dinaphthopyran, 3-ethyl-spiro-dinaphthopyran, 3-phenyl-spiro-dinaphthopyran, 3-benzyl-spiro-dinaphthopyran, 3-methyl-naphtho-(6'-methoxybenzo)spiropyran and 3-propyl-spirodibenzopyran; lactam dyes such as Rhodamine B anilinolactam, Rhodamin (p-nitroanilino)lactam and Rhodamin (o-chloroanilino) lactam; and fluoran dyes such as 3-dimethylamino-7-methoxyfluoran, 3-diethylamino-6-methoxyfluoran, 3-diethylamino-7-methoxyfluoran, 3-diethylamino-7-chlorofluoran, 3-diethylamino-6-methyl-7-chlorofluoran, 3-diethylamino-6,7-dimethylfluoran, 3-(N-ethyl-p-toluidino)-7-methylfluoran, 3-diethylamino-7-N-acetyl-N-methylaminofluoran, 3-diethylamino-7-N-methylaminofluoran, 3-diethylamino-7-dibenzylaminofluoran, 3-diethylamino-7-N-methyl-N-benzylaminofluoran, 3-diethylamino-7-N-chloroethyl-N-methylaminofluoran, 3-diethylamino-7-N-diethylaminofluoran, 3-(N-ethyl-p-toluidino)-6-methyl-7-phenylaminofluoran, 3-(N-ethyl-p-toluidino)-6-methyl-7-(p-toluidino)fluoran, 3-diethylamino-7-(2-carbomethoxyphenylamino)fluoran, 3-(N-cyclohexyl-N-methylamino)-6-methyl-7-phenylaminofluoran, 3-pyrrolidino-6-methyl-7-phenylaminofluoran, 3-piperidino-6-methyl-7-phenylaminofluoran, 3-diethylamino-6-methyl-7-xylidinofluoran, 3-diethyl-amino-7-(o-chlorophenylamino)fluoran, 3-dibutylamino-7-(o-chlorophenylamino)fluoran, 3-pyrrolidino-6-methyl-7-p-butylphenylaminofluoran, 3-diethylamino-6-methyl-7-anilinofluoran, 3-dibutylamino-6-methyl-7-anilinofluoran and 3-(N-ethyl-N-isoamyl)amino-6-methyl-7-anilinofluoran. The amount of the leuco compound is 1 to 30 % by weight, preferably 5 to 20 % by weight, based on the total solid in the coating liquid for forming the heat-sensitive recording layer.

Various organic acids are known for coloring the leuco compound under heating. Examples of them include phenolic compounds such as 4-tert-butylphenol, 4-hydroxydiphenoxide, α -naphthol, β -naphthol, 4-hydroxyacetophenol, 4-tert-octylcatechol, 2,2'-dihydroxydiphenol, 2,2'-methylenebis(4-methyl-6-tert-isobutylphenol), 4,4'-isopropylidenebis(2-tert-butylphenol), 4,4'-sec-butylidenediphenol, 4-phenylphenol, 4,4'-isopropylidenediphenol (bisphenol A), 2,2'-methylenebis(4-chlorophenol), hydroquinone, 4,4'-cyclohexylidenediphenol, benzyl 4-hydroxybenzoate, dimethyl 4-hydroxyphthalate, hydroquinone monobenzyl ether, novolak-type phenolic resin and phenolic polymers; aromatic carboxylic acids such as benzoic acid, p-tert-butylbenzoic acid, trichlorobenzoic acid, terephthalic acid, 3-sec-butyl-4-hydroxybenzoic acid, 3-cyclohexyl-4-hydroxybenzoic acid, 3,5-dimethyl-4-hydroxybenzoic acid, salicylic acid, 3-isopropyl-salicylic acid, 3-tert-butylsalicylic acid, 3-benzylsalicylic acid, 3-(α -methylbenzyl)salicylic acid, 3-chloro-5-(α -methylbenzyl)salicylic acid, 3,5-di-tert-butylsalicylic acid, 3-phenyl-5-(α , α -dimethylbenzyl)salicylic acid and 3,5-di- α -methylbenzylsalicylic acid; and salts of these phenolic compounds or aromatic dicarboxylic acids with polyvalent metals such as zinc, magnesium, aluminum, calcium, titanium, manganese, tin and nickel.

The amount of the organic acid is 1 to 50 % by weight, preferably 5 to 40 % by weight, based on the total solid in the coating liquid for forming the heat-sensitive recording layer.

The ratio of the leuco compound to the organic acid substance in the heat-sensitive recording layer is suitably determined depending on the varieties of the leuco compound and organic acid used. Usually, 1 to 50 parts by weight, preferably 1 to 10 parts by weight, of the organic acid is used per part by weight of the leuco compound.

The coating liquid containing these substances is usually prepared by dispersing the leuco dye and the

organic acid together or separately from each other in water used as the dispersion medium with a mixer/pulverizer such as a ball mill, attritor or sand grinder. The size of the dispersed particles is desirably as small as possible. In particular, it is 2 μ m or less.

The coating liquid contains about 10 to 40 % by weight, preferably 15 to 30 % by weight, based on the total solid, of an adhesive such as a starch, hydroxyethyl cellulose, methyl cellulose, carboxymethyl cellulose, gelatin, casein, acacia, polyvinyl alcohol, diisobutylene/maleic anhydride copolymer salt, styrene/maleic anhydride copolymer salt, ethylene/acrylic acid copolymer salt, styrene/acrylic acid copolymer salt and an emulsion of styrene/butadiene copolymer.

Further, the coating liquid can contain various assistants such as dispersants, e.g. sodium dioctylsulfosuccinate, sodium dodecylbenzenesulfonate, sodium salt of lauryl sulfate, alginic acid salts and metal salts of fatty acids; ultraviolet ray absorbers such as benzophenone compounds and triazole compounds; anti-foaming agents; fluorescent dyes; colorants; and dyes.

The coating liquid can contain, if necessary, lubricants such as zinc stearate, calcium stearate, polyethylene wax, carnauba wax, paraffin wax and ester wax; inorganic pigments such as kaolin, clay, talc, calcium carbonate, calcined clay, titanium oxide, diatomaceous earth, fine particles of anhydrous silica and activated clay; and sensitizers such as stearamide, stearic methylenebisamide, oleic amide, palmitic amide, spermoleic amide, coconut fatty acid amides, m-terphenyl, p-benzylbiphenyl, ester derivatives of hydroxynaphthoic acid, dibenzyl terephthalate and tribenzylamine.

The method of forming the heat-sensitive layer of the heat-sensitive recording paper of the present invention is not particularly limited and any method known in the art can be employed. For example, the coating liquid can be applied by air-knife coating or blade coating method and then the coating film is dried. Although the amount of the coating liquid to be applied is not particularly limited, it is usually 2 to 12 g/m² (on dry basis), preferably 3 to 10 g/m².

As described above, the present invention is characterized in that the electric resistance of the back of the heat-sensitive recording paper is lowered to a specified value by the treatment. In the present invention, such a treatment is conducted by a method wherein the agent of the present invention for lowering the electric resistance is applied to the back of the recording medium after the formation of the heat-sensitive recording layer or a method wherein the agent is previously applied to the base paper.

The guanidine salts usable for forming the agent of the present invention for lowering the electric resistance include water-soluble, organic or inorganic guanidine/acid adduct salts and guanidine derivative salts. Examples of the guanidine/acid adduct salts include guanidine hydrochloride, guanidine nitrate, guanidine carbonate, guanidine phosphate, guanidine tetraborate, guanidine sulfate and guanidine sulfamate. Guanidine hydrochloride is particularly preferred, since it has a high water solubility and excellent effect of increasing the electroconductivity per a unit weight thereof. An example of the guanidine derivative salts is guanidine hydrochloride/ethylene oxide adduct. The content of the guanidine salts or their derivatives in the agent for lowering the electric resistance is preferably 0.5 to 50 wt %, more preferably 1 to 20 wt %. The agent contains a balance of water and may further contain additives mentioned below.

Although the present invention may use the guanidine salts or the guanidine derivative salts singly, it is preferable that the guanidine salts or the guanidine derivative salts be used together with cationic polymers having a quaternary ammonium group. The examples of the cationic polymers include homopolymers of vinyl monomers containing a quaternary ammonium group and copolymers thereof with another vinyl monomer.

The polymers usable herein are preferably acrylic polymers and styrene polymers.

The acrylic polymers include, for example, copolymers of a quaternized monomer such as quaternized dialkylaminoethyl methacrylate, quaternized dialkylaminoethyl acrylate, quaternized dialkylaminoethyl methacrylamide or quaternized dialkylaminoethyl acrylamide with a monomer such as an acrylic ester, acrylamide, vinyl acetate, vinyl chloride, vinylidene chloride, styrene or acrylonitrile. An example of them is poly(2-methacryloxyethyltrimethylammonium chloride).

The styrene polymers include homopolymers of styrene or α -methylstyrene having a quaternary ammonium group and copolymers of them with the above-described copolymerizable components. An example of them is poly(vinylbenzyltrimethylammonium chloride).

The tertiary amino group can be quaternized with, for example, dimethylsulfuric acid, hydrochloric acid, acetic acid, benzyl chloride, epichlorohydrin and ethylene oxide. Among them, dimethylsulfuric acid is particularly preferred.

The molecular weight of the copolymers is about 30,000 to 1,000,000, preferably 100,000 to 300,000. The molecular weight is thus limited, because when it is less than 30,000, the formed dry coating film is weak and blocking is caused and, on the contrary, when it exceeds 1,000,000 the compatibility thereof with the guanidine salt is poor.

Although the quaternary ammonium group content of the copolymer is not limited, it is preferably at least 30 molar % and it may partially contain a tertiary amino group.

Thus the agent of the present invention for lowering electric resistance comprises, as the indispensable components, a guanidine salt or guanidine derivative salt singly or in combination with a polymer containing a quaternary ammonium group. In addition, it may contain various cationic high polymers.

The electric resistance of guanidine salts varies in a high degree depending on the humidity. It is particularly high at a low humidity. On the contrary, the humidity-dependence of the cationic polymer having a quaternary ammonium group is lower than that of the guanidine salt. Therefore, the mixing ratio of the guanidine salt or guanidine derivative salt to the cationic polymer having a quaternary ammonium group varies depending on the electrostatic properties of the support, the environment in which the heat-sensitive paper is mainly used, and conditions of the recording machine, particularly the electro-conductivity of the platen roll conveying speed thereof. The weight ratio of the guanidine salt to the polymer is usually 99:1 to 1:99, preferably 95:5 to 5:95. Further, additives such as a rust preventive can be used in an amount of 0.01 to 1 % by weight, preferably 0.05 to 0.5 % by weight, based on the total solid in the agent.

The agent for lowering the electric resistance is applied in an amount of 0.05 to 5 g/m² (on dry basis), preferably 0.1 to 2 g/m², to the back of the supporter having the heat-sensitive recording layer of the present invention. The surface electric resistance of the back of the heat-sensitive recording medium is 5×10^5 to $5 \times 10^{13} \Omega$ as determined at a temperature of 20 °C and at a relative humidity of 20 %. The reason why the electric resistance is limited to $5 \times 10^5 \Omega$ or above is that when it is less than this value, the agent for lowering the electric resistance is required in a large amount and problems such as blocking are posed.

According to the present invention, there is provided the heat-sensitive recording medium having a low electric resistance which is free from troubles in feeding or discharging thereof from the recording machine and free from the fog of background and does not cause impairment of the thermal head.

The following Examples will further illustrate the present invention.

Example 1

Preparation of heat-sensitive paint:

Liquid A:

Black basic leuco dye; 3-(N-ethyl-N-isoamyl)-

amino-6-methyl-7-anilino-fluoran

(S-205; a product of Yamada Kagaku Co.) 9 parts by weight

12 % Aqueous polyvinyl alcohol solution 15 parts by weight

20 % Aqueous ammonium polystyreneacrylate

	solution	0.7 parts by weight
	Water	30 parts by weight
5	<u>Liquid B:</u>	
	2,2-Bis(4-hydroxyphenyl)propane	20 parts by weight
10	m-Terphenyl	20 parts by weight
	12 % aqueous polyvinyl alcohol solution	50 parts by weight
	20 % aqueous ammonium polystyreneacrylate	
15	solution	3 parts by weight
	Water	62.3 parts by weight

20

Each of the Liquids A and B was treated with a sand grinder to reduce the average particle diameter of the dispersed particles to 2 μ m or less.

25

	<u>Liquid C:</u>	
	Calcium carbonate	25 parts by weight
30	40 % aqueous sodium polyacrylate solution	1 part by weight
	water	24 parts by weight

35 The liquid C was treated with a homomixer for 10 min.

54.7 parts by weight of the liquid A, 155.3 parts by weight of the liquid B and 50 parts by weight of the liquid C prepared as described above were mixed together. 33.3 parts by weight of 30 % zinc stearate dispersion, 100 parts by weight of 12 % aqueous polyvinyl alcohol solution and 130 parts by weight of water were added to the obtained mixture to form a heat-sensitive paint.

40 The heat-sensitive paint was applied to a wood-free base paper having a basis weight of 50 g/m² in an amount of 5 g/m² (on dry basis) and then dried to prepare a heat-sensitive recording paper.

5 % Aqueous solution (Resistance-lowering agent 1 of the present invention) containing guanidine hydrochloride was applied to the back of the heat-sensitive recording paper thus obtained in an amount of 0.5 g/m² (on dry basis) and then dried. It was then subjected to super calender treatment to prepare a heat-sensitive recording paper.

45 Guanidine hydrochloride used in this Example was prepared by adding hydrochloric acid to guanidine.

Example 2

50 A heat-sensitive recording paper was prepared in the same manner as that of Example 1 except that 5 % aqueous solution (Resistance-lowering agent 2 of the present invention) containing guanidine nitrate was applied to the back of the heat-sensitive recording paper and then dried and it was subjected to the super calender treatment. Guanidine nitrate used in this Example was prepared by adding nitric acid to guanidine.

55 Example 3

A heat-sensitive recording paper was prepared in the same manner as that of Example 1 except that 5 % aqueous solution (Resistance-lowering agent 3 of the present invention) containing guanidine carbonate

was applied to the back of the heat-sensitive recording paper and then dried and it was subjected to the super calender treatment.

Example 4

5

A heat-sensitive recording paper was prepared in the same manner as that of Example 1 except that 5 % aqueous solution (Resistance-lowering agent 4 of the present invention) containing guanidine phosphate was applied to the back of the heat-sensitive recording paper and then dried and it was subjected to the super calender treatment. Guanidine phosphate used in this Example was prepared by adding phosphoric acid to guanidine.

10

Example 5

A heat-sensitive recording paper was prepared in the same manner as that of Example 1 except that 15 % aqueous solution (Resistance-lowering agent 5 of the present invention) containing guanidine sulfate was applied to the back of the heat-sensitive recording paper and then dried and it was subjected to the supercalender treatment. Guanidine sulfate used in this Example was prepared by adding sulfuric acid to guanidine.

15

20 Example 6

A heat-sensitive recording paper was prepared in the same manner as that of Example 1 except that 5 % aqueous solution (Resistance-lowering agent 6 of the present invention) containing guanidine sulfamate was applied to the back of the heat-sensitive recording paper and then dried and it was subjected to the super calender treatment. Guanidine sulfamate used in this Example was prepared by adding sulfamic acid to guanidine.

25

Example 7

A heat-sensitive recording paper was prepared in the same manner as that of Example 1 except that 30 % aqueous solution (Resistance-lowering agent 7 of the present invention) containing ethylene oxide adducted guanidine hydrochloride was applied to the back of the heat-sensitive recording paper and then dried and it was subjected to the super calender treatment. Ethylene oxide adducted guanidine hydrochloride used in this Example was prepared by adding hydrochloric acid to ethylene oxide adducted guanidine.

30

35

Example 8

A heat-sensitive recording paper was prepared in the same manner as that of Example 1 except that 5 % aqueous solution (Resistance-lowering agent 8 of the present invention) containing guanidine hydrochloride and acrylic polymer having a quaternary ammonium in a weight ratio of 80:20 was applied to the back of the heat-sensitive recording paper thus obtained in an amount of 0.5 g/m² (on dry basis) and then dried. It was then subjected to super calender treatment to prepare a heat-sensitive recording paper.

40

The acrylic polymer used in this Example had a molecular weight of about 60,000 and the replacement of the quaternary ammonium was 40 molar %. Guanidine hydrochloride was prepared by adding hydrochloric acid to guanidine.

45

Example 9

A heat-sensitive recording paper was prepared in the same manner as that of Example 8 except that 50 % aqueous solution (Resistance-lowering agent 9 of the present invention) containing guanidine hydrochloride and acrylic polymer having a quaternary ammonium in a weight ratio of 90:10 was applied to the back of the heat-sensitive recording paper and then dried and it was subjected to the super calender treatment.

50

Example 10

55

A heat-sensitive recording paper was prepared in the same manner as that of Example 8 except that 3 % aqueous solution of the Resistance-lowering agent 8 used in Example 8 was applied in an amount of 0.9 g/m² (on dry basis).

Example 11

A heat-sensitive recording paper was prepared in the same manner as that of Example 8 except that 5 % aqueous solution (Resistance-lowering agent 10 of the present invention) containing ethylene oxide adducted guanidine hydrochloride and acrylic polymer having a quaternary ammonium group in a weight ratio of 90:10 was applied to the back of the heat-sensitive recording paper and then dried and it was subjected to the super calender treatment.

Example 12

A heat-sensitive recording paper was prepared in the same manner as that of Example 8 except that 4 % aqueous solution (Resistance-lowering agent 11 of the present invention) containing guanidine hydrochloride and styrene polymer having a quaternary ammonium group in a weight ratio of 80:20 was applied to the back of the heat-sensitive recording paper and then dried and it was subjected to the super calender treatment.

The molecular weight of the styrene polymer was about 100,000 and the quaternary ammonium replacement was 35 molar %.

Comparative Example 1

A heat-sensitive recording paper was prepared in the same manner as that of Example 1 except that the Resistance-lowering agent 1 of the present invention was replaced with 5 % aqueous solution of sodium chloride (an inorganic salt) so as to coat it in an amount of 0.5 g/m² (on dry basis).

Comparative Example 2

A heat-sensitive recording paper was prepared in the same manner as that of Example 1 except that the Resistance-lowering agent 1 of the present invention used in Example 1 was replaced with 5 % aqueous solution of polyvinylbenzyltrimethylammonium chloride which is a cationic polymeric electrolyte so as to coat it in an amount of 0.5 g/m² (on dry basis).

Comparative Example 3

A heat-sensitive recording paper was prepared in the same manner as that of Example 1 except that the Resistance-lowering agent 1 of the present invention used in Example 1 was replaced with 5 % aqueous solution of polyethylene glycol monolaurate which is a nonionic polymer so as to coat it in an amount of 0.5 g/m² (on dry basis).

Comparative Example 4

A heat-sensitive recording paper was prepared in the same manner as that of Example 1 except that the Resistance-lowering agent 1 of the present invention used in Example 1 was replaced with salt-free water so as to coat it in amount of 10 ml/m².

Comparative Example 5

A heat-sensitive recording paper was prepared in the same manner as that of Example 1 except that the Resistance-lowering agent 1 of the present invention used in Example 1 was replaced with 5 % aqueous solution of sodium polystyrenesulfonate which is an anionic polymeric electrolyte so as to coat it in an amount of 0.5 g/m² (on dry basis).

The heat-sensitive recording papers prepared in Examples 1 to 12 and Comparative Examples 1 to 5 were subjected to the following tests to obtain the results shown in Tables 1 and 2.

(1) Storability:

A test pattern was printed with a heat-sensitive facsimile FF 621 C (a product of Fujitsu, Ltd.), and a background density and a density of the printed part were determined with Macbeth Densitometer RD-514. Further samples obtained by printing with FF 621 C were subjected to the following storability tests:

Before storage, the background density of all Examples and Comparative Examples is 0.06 except for 0.07 in Example 10, whereas the density of the printed part of all Examples and Comparative Examples

is 1.25 except for 1.24 in Example 9 and 1.26 in Example 10.

a) Humidity resistance:

The samples were kept at 40 °C at a high relative humidity of 90 % for 24 h and then the background density and the density of printed part were determined with Macbeth RD-514.

b) Heat resistance:

The samples were kept under a high-temperature drying condition (60 °C) for 24 h and then the background density and the density of printed part were determined with Macbeth RD-514.

(2) Head breakage test:

Commercially available Kyosera thermal head (KJT-216-8MGFI) was used. The heat-sensitive recording paper was wound round the platen roll. The platen roll and thermal head were fixed (0.15 kgf/cm) and placed under environmental conditions of 80 °C - 85 % RH. The head was impressed and kept under these conditions for 20 h. After solid printing, dot omission rate thereof was examined.

Evaluation:

○ : Dot omission rate was not higher than 5 %.

△ : Dot omission rate was 5 to 10 %.

× : Dot omission rate was higher than 10 %.

(3) Surface electric resistance:

The surface electric resistance was determined with 4329 A HIGH RESISTANCE METER and 16008A RESISTIVITY CELL (products of Yokokawa Hewlett-Packard co.) at 20 °C in an atmosphere of 20 % RH.

(4) Passability test:

30 sheets were continuously printed to examine paper stoppage and stacking properties. In the test, a commercially available FAX Rifax 700S (a product of Ricoh Co., Ltd.) and Facsimile test chart No. 2 (a product of Gazo Denshi Gakkai) were used at 20 °C in an atmosphere of 20 % RH.

Table 1

		Surface electric resistance (20°C 20%KH) Ω	Head break- age test	Paper pass- abili- ty
Example	1	9.5×10^{11}	○	○
	2	8.4×10^{12}	○	○
	3	1.5×10^{12}	○	○
	4	5.6×10^{12}	○	○
	5	3.1×10^{12}	○	○
	6	1.1×10^{12}	○	○
	7	7.3×10^{12}	○	○
	8	4.6×10^{10}	○	○
	9	7.5×10^{11}	○	○
	10	2.2×10^{11}	○	○
	11	5.8×10^{10}	○	○
	12	1.4×10^{11}	○	○
Com- parative Example	1	6.0×10^{13}	×	△
	2	1.0×10^{12}	○	○
	3	4.7×10^{11}	○	○
	4	1.5×10^{14}	○	×
	5	6.3×10^{11}	×	○

Table 2

		Storability test			
		Humidity resistance		Heat resistance	
		Back-ground	Printed part	Back-ground	Printed part
Example	1	0.08	1.20	0.12	1.24
	2	0.08	1.19	0.12	1.22
	3	0.09	1.24	0.12	1.21
	4	0.09	1.22	0.12	1.24
	5	0.08	1.19	0.13	1.20
	6	0.08	1.21	0.11	1.24
	7	0.08	1.22	0.12	1.23
	8	0.08	1.19	0.12	1.23
	9	0.09	1.17	0.14	1.23
	10	0.09	1.20	0.12	1.24
	11	0.09	1.20	0.13	1.24
	12	0.08	1.21	0.11	1.22
Com-parative Example	1	0.10	1.18	0.13	1.22
	2	0.24	1.15	0.33	1.23
	3	0.06	0.61	0.07	0.70
	4	0.07	1.20	0.14	1.21
	5	0.08	1.17	0.11	1.20

Claims

1. A heat-sensitive recording medium which comprises, on a support, a heat-sensitive recording layer comprising a leuco compound and an organic acid capable of coloring upon contact with the leuco compound, wherein the back of the support is coated with an agent for lowering the electric resistance comprising a guanidine salt or guanidine derivative salt.

2. A heat-sensitive recording medium according to claim 1 wherein thus-coated back of the support has a surface electric resistance of 5×10^5 to $5 \times 10^{13} \Omega$ at 20°C at a relative humidity of 20 %.
3. A heat-sensitive recording medium according to claim 1 or 2 wherein the guanidine salt is selected from the group consisting of water-soluble acid adduct salts of guanidine and guanidine derivatives.
4. A heat-sensitive recording medium according to claim 3 wherein the guanidine salt is selected from the group consisting of water-soluble inorganic and organic salts.
5. A heat-sensitive recording medium according to claim 1 or 2 wherein the guanidine salt is selected from the group consisting of guanidine hydrochloride, guanidine nitrate, guanidine carbonate, guanidine phosphate, guanidine tetraborate, guanidine sulfate and guanidine sulfamate.
6. A heat-sensitive recording medium according to claim 1 or 2 wherein the guanidine salt is guanidine hydrochloride.
7. A heat-sensitive recording media according to any one of claims 1 to 6 wherein the agent for lowering the electric resistance comprising a guanidine salt or guanidine derivative salt in an amount of 0.5 to 50 wt % and the balance of water.
8. A heat-sensitive recording medium according to any one of claims 1 to 7 wherein the agent for lowering the electric resistance is coated on the back of the support in an amount of 0.05 to 5 g/m².
9. A heat-sensitive recording medium according to any one of claims 1 to 8 wherein the agent for lowering the electric resistance further comprises a cationic polymer having a quaternary ammonium group.
10. A heat-sensitive recording medium according to claim 9 wherein the cationic polymer having a quaternary ammonium group is selected from homopolymers of vinyl monomers having a quaternary ammonium group or copolymers thereof with another vinyl monomer.
11. A heat-sensitive recording medium according to claim 9 wherein the cationic polymer is acrylic polymers having a quaternary ammonium group.
12. A heat-sensitive recording medium according to claim 11 wherein the acrylic polymer is selected from the group consisting of copolymers of a quaternized dialkylaminoethyl methacrylate, quaternized dialkylaminoethyl acrylate and quaternized monomeric derivatives thereof with an acrylic ester, acrylamide, vinyl acetate, vinyl chloride, vinylidene chloride, styrene or acrylonitrile.
13. A heat-sensitive recording medium according to claim 11 or 12 wherein the acrylic polymer is poly(2-mechacryloxyethyltrimet hylammonium chloride).
14. A heat-sensitive recording medium according to any one of claims 9 to 13 wherein the cationic polymer having a quaternary ammonium group is styrene polymers.
15. A heat-sensitive recording medium according to claim 14 wherein the styrene polymer is selected from the group consisting of homopolymers of styrene or α -methylstyrene having a quaternary ammonium group and copolymers of them with an acrylic ester, acrylamide, vinyl acetate, vinyl chloride, vinylidene chloride, styrene or acrylonitrile.
16. A heat-sensitive recording medium according to claim 14 or 15 wherein the styrene polymer is poly-(vinylbenzyltrimethylammonium chloride).
17. A heat-sensitive recording medium according to any one of claims 9 to 16 wherein a mixing ratio of the guanidine salt or guanidine derivative salt to the cationic polymer having a quaternary ammonium group is from 99:1 to 1:99 by the weight ratio.
18. A heat-sensitive recording medium according to any one of claims 9 to 17 wherein the agent for lowering the electric resistance is applied to the back of the support in an amount of 0.05 to 5 g/m² (on

dry basis) .

5

10

15

20

25

30

35

40

45

50

55



European
Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 10 1130

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	PATENT ABSTRACTS OF JAPAN vol. 7, no. 50 (M-197)(1195) 26 February 1983, & JP-A-57 199687 (MITSUBISHI SEISHI K.K.) 07 December 1982, * the whole document * - - -	1-18	B 41 M 5/40
A	PATENT ABSTRACTS OF JAPAN vol. 13, no. 183 (M-820)(3531) 28 April 1989, & JP-A-01 11883 (OJI PAPER COMPANY LIMITED) 17 January 1989, * the whole document * - - -	1-18	
A	PATENT ABSTRACTS OF JAPAN vol. 13, no. 154 (M-814)(3502) 14 April 1989, & JP-A-63 315286 (RICOH K.K.) 22 December 1988, * the whole document * - - -	1-18	
A	PATENT ABSTRACTS OF JAPAN vol. 11, no. 218 (M-607)(2665) 15 July 1987, & JP-A-62 33673 (RICOH K.K.) 13 February 1987, * the whole document * - - -	1-18	
A	PATENT ABSTRACTS OF JAPAN vol. 11, no. 215 (M-606)(2662) 11 July 1987, & JP-A-62 32080 (RICOH K.K.) 12 February 1987, * the whole document * - - - - -	1-18	
The present search report has been drawn up for all claims			
Place of search		Date of completion of search	Examiner
The Hague		30 August 91	BACON,A.J.
<div>CATEGORY OF CITED DOCUMENTS</div> <div>X : particularly relevant if taken alone</div> <div>Y : particularly relevant if combined with another document of the same category</div> <div>A : technological background</div> <div>O : non-written disclosure</div> <div>P : intermediate document</div> <div>T : theory or principle underlying the invention</div> <div>E : earlier patent document, but published on, or after the filing date</div> <div>D : document cited in the application</div> <div>L : document cited for other reasons</div> <div>& : member of the same patent family, corresponding document</div>			

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

☐ BLACK BORDERS

☒ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES

☒ FADED TEXT OR DRAWING

☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING

☐ SKEWED/SLANTED IMAGES

☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS

☐ GRAY SCALE DOCUMENTS

☒ LINES OR MARKS ON ORIGINAL DOCUMENT

☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY

☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.